METAL 2022

SEPTEMBER 5–9, 2022
HELSINKI, FINLAND

PROCEEDINGS OF THE INTERIM MEETING OF THE ICOM-CC METALS WORKING GROUP

EDITED BY PAUL MARDIKIAN, LIISA NÄSÄNEN, AND AKI ARPONEN

ICOM-CC
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Proceedings and user interface design and production: Eduardo Pulido (epulido@sapo.pt)

Copy editing: Carla Nunes (carlarnunes@gmail.com), Per Christopher Foster (chris.foster@netcabo.pt), and Wendy Ran (ran.wendy@gmail.com)

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Cover image: Viking Age swords found in Finland, now in the Archaeological Collections of the Finnish Heritage Agency. The hilts in Viking Age swords are true masterworks of metal technology. The mythical animals and palmettes in the hilt of KM10833:1 (front cover, left) were created with gilt silver and niello; in the pommel of KM9243:1 (back cover, right), copper and silver wires weave a herringbone motif. © Finnish Heritage Agency

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POSTER SESSION

Analysis of Heterogeneous Tarnish on Silver-based Alloys Using the Pleco for Local, Controlled Electrolytic Cleaning

Nicola Ricotta*
Department of History, Archaeology, Geography, Fine and Performing Arts (SAGAS), University of Florence
Florence, Italy
nicola.ricotta@unifi.it
www.sagas.unifi.it

Andrea Cagnini
Opificio delle Pietre Dure (OPD)
Florence, Italy
andrea.cagnini@beniculturali.it
www.opificiodellepietredure.it

Christian Degrigny
Haute Ecole Arc Conservation-restauration (HE-Arc CR), HES-SO University of Applied Sciences and Arts Western Switzerland
Neuchâtel, Switzerland
christian.degrigny@he-arc.ch
www.he-arc.ch

*Author for correspondence

Abstract
Artworks made of silver-based alloys tarnish unevenly, which considerably compromises their surface appearance as well as their historical and artistic value. Mechanical and chemical cleaning methods remove silver tarnish but in some cases are difficult to control. Electrolytic processes, which are often preferred because they retain some of the constituent materials, require an appropriate protocol to avoid side effects such as overcleaning and black spots. Using the representative example of a heterogeneously tarnished silver-based artwork, we demonstrate the potential of the Pleco electrolytic pencil to identify the nature of the tarnish. Artificial coupons mimicking the artwork were employed to optimise the use of the Pleco in the local, controlled cleaning of metal surfaces.

Keywords
silver-alloy, heterogeneous tarnish, Pleco®, artificial coupon, linear sweep voltammetry, analysis

Introduction

The tarnishing of silver-based objects is a common problem faced by conservation professionals. The metal surface tarnishes unevenly, with the colour varying from yellow to black depending on the thickness of the tarnish. In addition, the composition of the alloy, the environment and previous conservation interventions influence the nature and appearance of the alteration. The main components of silver tarnish are silver sulfide (Ag_2S) and silver chloride (AgCl), but the presence of other elements in the alloy, such as copper, leads to the formation of other compounds (Cu_2O, Cu_2S, etc.) (Costa 2001).

Local identification of the silver tarnish is crucial to appreciate its heterogeneity and the likely composition of the underlying metal but also to define appropriate cleaning protocols. The Pleco electronic pencil was developed in 2016 by the Haute Ecole Arc Conservation-restauration in Neuchâtel and has proved to be a versatile tool for the analysis and local cleaning of silver tarnish. Unlike conventional cleaning methods, it also allows the reduction of silver tarnish. Linear scanning voltammetry (LSV) is used to identify tarnish compounds based on their reduction peaks and then to define treatment parameters (Degrigny et al. 2016).

The Pleco pencil is expected to solve the problem of overcleaning of heterogeneously tarnished silver surfaces during electrolytic immersion cleaning. Overcleaning occurs because: (i) the same treatment parameters are applied to the whole metal surface and (ii) the polarisation of less tarnished areas is similar to that of heavily tarnished ones, causing hydrogen to be released from the former and resulting in excessive cleaning. Furthermore, black spots due to the reduction of copper compounds may appear (Ricotta et al. 2019). The Pleco, however, works selectively and can clean differently tarnished metal surfaces as appropriate (Degrigny et al. 2015). Nonetheless, it poses a few technical problems for end users. For example, the identification of small reduction peaks on LSV plots is difficult due to their masking by current fluctuations. These fluctuations are caused by the pumping system, which heterogeneously supplies and extracts the electrolyte on the metal surface.

Our approach

The objective in this research was to further optimise the use of the Pleco as an analytical tool allowing correct tarnish reduction for local, controlled cleaning.

Valadier case study

The Valadier cooler, made by the Roman silversmith Giuseppe Valadier in 1810, is part of the collection of Gallerie degli Uffizi, Tesoro dei Granduchi in Florence (Inv. Pitti Art Objects (1911) n. 1838). It depicts mythological scenes (Figure 1a) and consists of a body, handles and a base, all made by casting from a silver alloy. The object has decorations in relief that have been chased and both polished and matt surface finishes have been applied. Silver-alloy foils have been embossed to fit inside the cooler and its base. All elements are secured by a central bolt and nut. Non-invasive X-ray fluorescence (XRF) analyses, performed with the portable XRF spectrometer ELIO (XGLab) and without any preliminary surface cleaning, revealed that the elements of the cooler consist of different silver-copper alloys. Quantitative analysis results were obtained using bAxil BrightSpec software and a certified Ag% 92.44 ± 0.12 Cu% 7.59 ± 0.14 standard and were normalised to 100% (Table 1).

Like many objects in the museum's storage, the Valadier cooler is heterogeneously tarnished. As shown in Figure 1a, some parts of the body, handles and base are more tarnished (either the hollow parts or chased backgrounds, Figure 1b), while the polished figures and other reliefs seem to be only slightly tarnished (Figure 1c). The differences could be due to intentional depth effects or to regular maintenance of the object, as shown by the thick tarnish layers in some grooves that are more difficult to reach than the embossed surfaces. This condition demonstrated the importance of a more selective cleaning, such as is possible using the Pleco.

Figure 1. Valadier cooler: general view (a) and details of the scenes depicted on the body (b) with different levels of tarnish (c)

Table 1. XRF analysis of the different elements of the Valadier cooler

Measuring points		Ag%	Cu%	Trace elements
Inner upper plate	1	93.6 ± 0.1	6.4 ± 0.2	Zn
	2	94.1 ± 0.1	5.9 ± 0.2	Zn
Body	3	94.1 ± 0.1	5.9 ± 0.2	Zn and Fe
	4	95.0 ± 0.1	5.0 ± 0.2	Zn and Fe
	5	96.3 ± 0.1	3.7 ± 0.2	Zn and Fe
Handle	6	90.7 ± 0.1	9.3 ± 0.1	Zn, Fe and Pb
	7	90.4 ± 0.1	9.6 ± 0.1	None
Base	8	92.4 ± 0.1	7.6 ± 0.2	Zn and Pb
	9	90.0 ± 0.1	10.0 ± 0.1	None
Inner bottom plate	10	93.3 ± 0.1	6.7 ± 0.2	Zn
	11	92.4 ± 0.1	7.6 ± 0.1	Zn

Preliminary LSV plots performed with the Pleco on two discrete, randomly chosen areas (1 and 2), located opposite each other on the surface of the cooler body (Figure 2), showed the presence of different corrosion products. On one side, only silver compounds were detected, and on the other side additional copper compounds were found. This result suggested that the composition of the cooler body surface is not uniform. To confirm this hypothesis, smoother plots were required. Indeed, the high current fluctuations between −1 and −2V/GC (glassy carbon) prevented a correct visualisation of any small reduction peaks. However, one such peak may have been present on the plot of side 1, around −1.6V/GC (Figure 3).

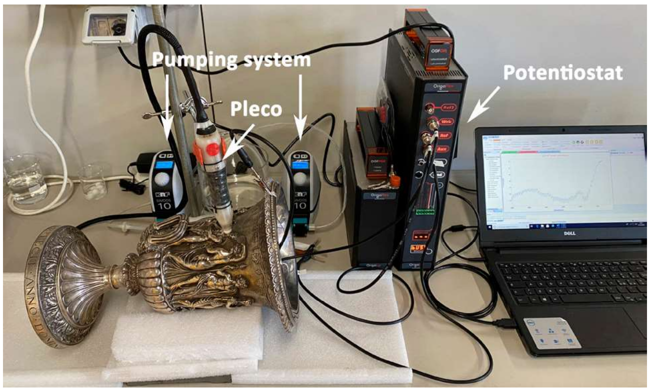

Figure 2. Electrolytic setup to obtain LSV plots of the body of the Valadier cooler using the Pleco

Electrochemical study of coupons simulating the Valadier cooler

To optimise the LSV plots, metal coupons made from sterling silver (Ag7.5%Cu) plates were used. Some were flat, matt and chased (4 × 2 cm, Figure 4a), and others were polished and curved (6 × 4 cm, Figure 4b).

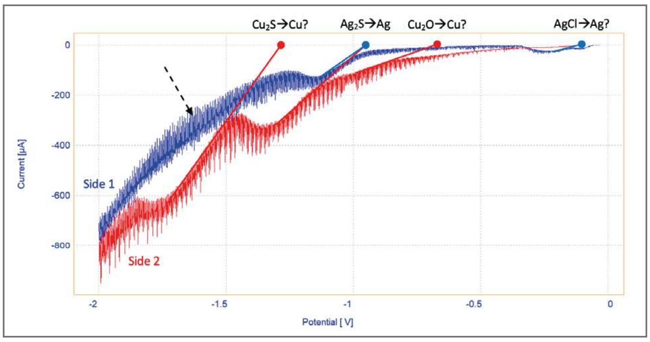

Figure 3. LSV plots of two sides of the Valadier cooler body. The different compounds are identified by the potentials located at the intersection between the tangents of the slopes of the reduction peaks and the potential axis. The reductions of AgCl, Cu_2O and Cu_2S are hypothetical. Note the possible presence of a peak on the blue plot around −1.6V/GC

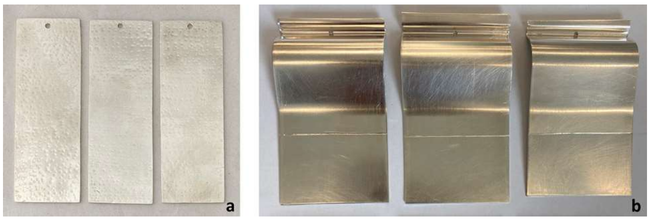

Figure 4. Metal coupons used to mimic the behaviour of the Valadier cooler: matt and chased (a) and polished and curved (b)

The metal coupons were artificially aged in a 24 h exposure to warm hard-boiled eggs, peeled and cut into four sections. The coupons, handled without gloves so as to induce the formation of fingerprints, quickly tarnished, acquiring a heterogeneous appearance ranging from yellow to blue (Figure 5).

Figure 5. Artificial tarnishing of the metal coupons in a desiccator using warm hard-boiled eggs, peeled and cut into four sections (a), and the surface of the coupons after a 24 h exposure (b)

LSV plots on the tarnished sterling silver plates (bluer areas) showed an electrochemical behaviour similar to that of body side 2 of the Valadier cooler (Figure 6). The same compounds appeared, although the maxima of the peaks of the Valadier cooler shifted to more negative potentials in areas of presumably thicker corrosion products.

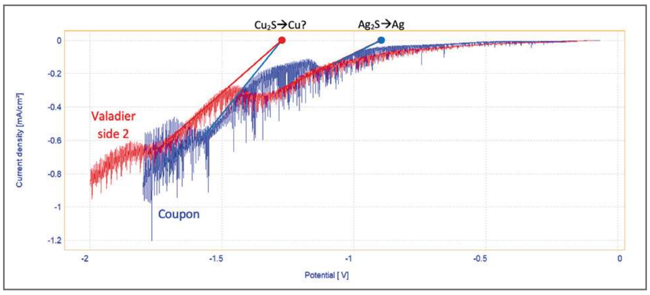

Figure 6. Comparison of the LSV plots on side 2 of the Valadier cooler body and the artificial coupon

As the artificial silver-based coupons correctly simulated the electrochemical behaviour of the Valadier cooler, they were employed to optimise the use of the Pleco.

Optimisation of the Pleco

Several parameters were studied to minimise the current fluctuations seen in the LSV plots:

- The circulation rates of the diaphragm pumps. If the extraction flow rate is too high, the Pleco's microporous polyvinyl formal (PVFM) pad dries out, reducing fluctuations, whereas if it is too low, the electrolyte leaks out of the pad and induces more fluctuations.
- A large pad (pad 1 in Figure 7) compressed when inserted into the Pleco nozzle causes smaller current fluctuations but also prevents electrolyte renewal on the metal surface. Conversely, a small pad promotes electrolyte renewal but also causes electrolyte leakage (pad 3 in Figure 7).
- By changing the shape of the pad (from flat, round, slightly sharp to conical; Figure 7), the contact surface with the metal surface is reduced, causing larger fluctuations of current that can be reduced by increasing the extraction flow rate.

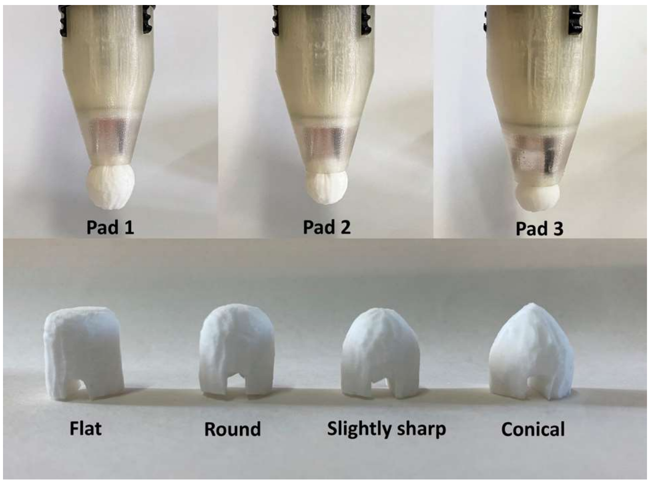

Figure 7. Different sizes and shapes of the tested pads, inserted in the nozzle of the Pleco

LSV plots on the Valadier case study

The best LSV plots were obtained with conically shaped pad 2 (medium size), which resulted in supply and extraction flow rates of 10 and 90, respectively. A total of nine LSV measurements were performed under these conditions on the Valadier cooler body. The studied areas, preliminarily degreased with alcohol and acetone, were randomly selected on sides 1 and 2, considering only the most tarnished surfaces and different surface finishes. Three measurements were made on polished areas and six on chased areas.

On side 1, the tarnish was shown to consist mainly of Ag_2S and AgCl (?) (Figure 8). On side 2, reduction peaks of Cu_2O (?) and Cu_2S (?) were also present (Figure 9).

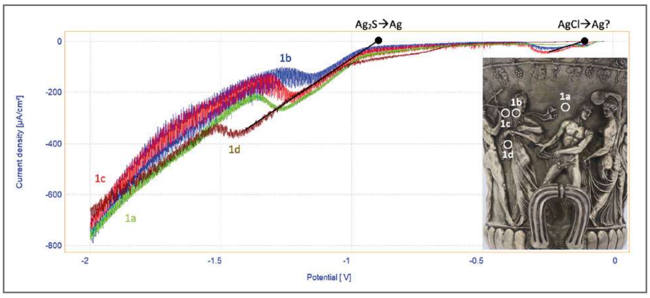

Figure 8. LSV plots on different areas of side 1 of the Valadier cooler body

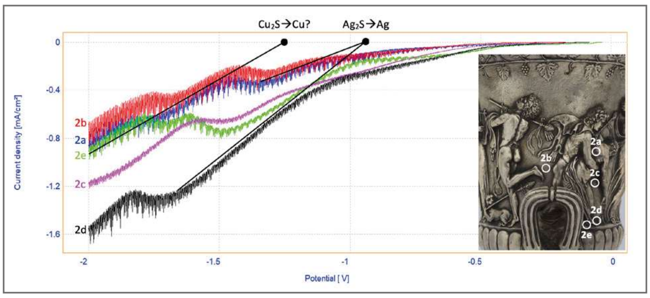

Figure 9. LSV plots on different areas of side 2 of the Valadier cooler body

These results suggested that the Valadier cooler body had been superficially treated during its production, to enrich its silver content. As a result of repeated tarnishing and cleaning interventions, part of the enrichment layer abraded, exposing the underlying metal. Why one side of the body was apparently differently preserved from the other is unknown.

To validate these results, further LSV measurements will be made, with the measurement areas chosen according to the different chromatic types of surface tarnish observed under binocular microscopy. This will allow mapping of the surface and the assignment of a specific composition to each aspect of the surface tarnish.

Conclusion

The Pleco device and the accompanying LSV plots are a valuable diagnostic tool, providing critical information on the tarnishing of silver-based objects. However, the accuracy of the analysis requires an understanding of the effects of the parameters that influence the presence of current fluctuations in the LSV plots. The Pleco pencil is perfectly adapted to the study of heterogeneous tarnish, but it is invasive, as the measurement point on the surface of the object where the reduction reactions occurred is visible. However, this disadvantage becomes secondary if cleaning the object after the diagnostic steps is planned.

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References

Costa, V. 2001. The deterioration of silver alloy and some aspects of their conservation. *Studies in Conservation* 46(suppl. 1): 18–34.

Degrigny, C., R. Jeanneret, and D. Witschard. 2015. Local cleaning with the Pleco electrolytic pencil of tarnished Saint Candide reliquary head at the Treasury of Saint-Maurice Abbey, Valais (Switzerland). *e-Preservation Science* 12: 20–27.

Degrigny, C., R. Jeanneret, D. Witschard, C. Baudin, G. Bussy, and H. Carrel. 2016. A new electrolytic pencil for the local cleaning of silver tarnish. *Studies in Conservation* 61(3): 162–73.

Ricotta, N., C. Degrigny, A. Cagnini, and C. Ortolani. 2019. Design of a suitable cleaning procedure for the tarnished silver elements of the reliquary bust of Santa Vittoria, Diocesan Museum of Agrigento, Sicily. In *Metal 2019: Proceedings of the Interim Meeting of the ICOM-CC Metals Working Group, Neuchâtel, 2–6 September 2019*, eds. C. Chemello, L. Brambilla, and E. Joseph, 261–64. Paris: International Council of Museums–Committee for Conservation (ICOM-CC) and Haute Ecole Arc Conservation-restauration (HE-Arc CR).

Authors

Nicola Ricotta is a conservator and PhD student at the University of Florence, Italy.

Andrea Cagnini is a chemist and professor at the Scuola di Alta Formazione e di Studio, Opificio delle Pietre Dure, Florence, Italy.

Christian Degrigny is an electrochemist and professor at the Haute Ecole Arc Conservation-restauration, Neuchâtel, Switzerland.

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